NATURAL LEVELS OF NICKEL, SELENIUM, AND ARSENIC IN THE SOUTHERN SAN FRANCISCO BAY AREA

for:

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Environmental Services Department**

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30 June 1998

EXECUTIVE SUMMARY

This report is a summary of the results of a literature search for information on natural levels of nickel, selenium, and arsenic in the southern San Francisco Bay area. Relatively little has been published concerning the trace-element composition of bedrock and soil units or describing natural concentrations of these elements in sediment and water in and around the Bay. The information that has been published indicates a wide range of compositions, and there presently is not enough data to estimate average concentrations of trace elements in the region.

Some bedrock units in the south Bay area, especially serpentinite, contain high levels of Ni, up to 2700 ppm. Rocks such as marine shales and sulfide ore deposits that contain elevated levels of Se in other regions also are present, but local samples of these evidently have not been analyzed. Occurrences of rocks with high concentrations of As have not been reported in the area.

Streams, lakes, and groundwater in the south Bay area generally contain low natural levels of Ni, Se, and As. Studies in nearby regions suggest that Ni is transported largely on and in particles, Se is carried mostly in solution, and significant proportions of As are carried both in solution and associated with particles. A few analyses of stream sediment indicate Ni contents up to about 200 ppm and low Se and As contents, but stream sediment, especially suspended material, has not been studied in detail.

Natural levels of trace elements within the San Francisco Bay are difficult to assess from published data. Limited analyses of core samples suggest that natural background levels of Ni are about 80 to 90 ppm in the sediment. Post-depositional changes in natural sediment evidently release metals, creating a potentially important source of Ni within the Bay. Most analyses for Se and As are of recent materials that may be influenced by human activites, so the natural background levels of Se and As in the south Bay are difficult to specify based on published work.

INTRODUCTION

The purposes of this report are to summarize the current knowledge of natural levels of Ni, Se, and As in rocks, soils, sediment, and water of the southern San Francisco Bay area and to review studies of processes of transportation of these elements from the land to the water and sediment of the Bay. For the purposes of this report, the southern San Francisco Bay area is defined as the Bay south of the San Francisco - Oakland Bay Bridge and the land in the watershed area around it.

The information reported here is from published literature and other publicly available sources of previously released data. All data found in a literature search are reported, and no attempt was made to evaluate the quality of the analyses. Results are organized according to four geologically distinct groups of materials: bedrock and soil, stream and lake waters and sediment, ground water, and sediment and water within the San Francisco Bay.

BEDROCK AND SOIL

The bedrock geology of the southern San Francisco Bay area is summarized on maps compiled by Jennings (1977) and Wagner and others (1990). Bedrock units in the area include Mesozoic (225- to 66-million-year-old) sedimentary, metasedimentary, and metavolcanic rocks and serpentinite and Cenozoic (66-million-year-old and younger) sedimentary rocks and minor volcanic rocks. There are widespread areas underlain by loosely consolidated to unconsolidated, late-Cenozoic alluvial deposits, which are composed mostly of reworked fragments derived from the surrounding bedrock. Localized areas with potentially unusual trace-element concentrations include areas of mineralization, such as the New Almaden district (Bailey and Everhart, 1964), and sites of petroleum occurrence in the southwestern Santa Clara Valley (Stanley, 1995; Stanley and others, 1998).

Few analyses of trace element contents of rock and soil units in the southern San Francisco Bay area have been published. Boerngen and Shacklette (1981) reported analyses of three undescribed soil samples from the south Bay area, and Shacklette and Boerngen (1984) compared these results with similar analyses of more than 1300 samples of surficial materials collected throughout the conterminous United States. Scott (1995) reported background values of trace elements in uncontaminated, near-surface sediment from 25 locations in the vicinity of Moffett Federal Airfield in Mountain View. Kleinfelder, Inc. (1995) reported analyses of surface sediment and samples from 102 shallow soil borings along the Guadalupe River. Some of these sites evidently have been contaminated by human activities, but most of the samples apparently represent natural stream deposits. Burnett (1965) reported qualitative spectrochemical analyses of Ni and As in thirteen shale samples from the Diablo Range. The sections below summarize these and other available analyses, then address studies of the processes by which each trace element is released from rock to sediment and water.

Nickel

Boerngen and Shacklette (1981) reported Ni concentrations in soil samples from Gilroy, Palo Alto, and San Mateo County of 30 ppm (30 mg/kg), 30 ppm, and 70 ppm, respectively. All three of these values are higher than the nationwide geometric mean of 13 ppm Ni and fall within the highest of five ranges of Ni contents established by Shacklette and Boerngen (1984). Scott (1995) reported Ni values from 6 to 145 ppm, with an arithmetic average of 73.53 ppm, in 136 samples of sediment from Mountain View. All 136 samples that Scott included in her study contained measurable quantities of Ni. Kleinfelder, Inc. (1995) reported values from 40 to 900 ppm Ni in samples collected near the Guadalupe River. All samples had detectable Ni, and more than half had Ni contents higher than 100 ppm. The highest Ni concentration in a sample collected more than 5 ft below the ground surface was 460 ppm.

Published analyses of Ni contents in bedrock units in the southern Bay area include several for serpentinite, partially serpentinized ultramafic (high Mg and Fe) igneous rocks, and associated rocks, partly because these rocks are found in areas of economically significant mineral deposits. These rocks also have relatively high levels of Ni. Bailey and Everhart (1964) reported that both serpentinite and the altered and mineralized silica-carbonate rock associated with it in the New Almaden district contained 800 to 2000 ppm Ni. Serpentinized ultramafic rocks from the Red Mountain magnesite district, east of the Santa Clara Valley, were reported to contain 310 ppm Ni (0.04% NiO) by Bodenlos (1950) and 2500 to 2700 ppm Ni (0.32 to 0.35% NiO) by Himmelberg and Coleman (1968). The Red Mountain district is a small area in the upper watershed of Alameda Creek, but these analyses do show that local outcrops of serpentinite have relatively high concentrations of Ni. Parker (1967) reported that ultramafic rocks worldwide have an average Ni content of 2000 ppm, the highest of any common rock type, and Bailey and Blake (1974) showed that serpentinite throughout California also has high concentrations of Ni. Serpentinite is widespread in bedrock outcrops throughout the south Bay area (Wagner and others, 1990) and abundant as clasts in some late-Cenozoic gravels (Wills, 1995). Although analyses of these rocks apparently have not been published, the rocks are likely to have similarly high Ni contents.

Shale, chert, and graywacke sandstone are other abundant bedrock types in the south Bay area (Wagner and others, 1990). Burnett (1965) reported qualitative analyses of Ni in shale samples from the Diablo Range, with "trace" amounts found in all thirteen samples from the south Bay watershed. Mason and Moore (1982) estimated that average shale contains 68 ppm Ni. Chert from Marin County, which is closely related to chert in the south Bay (Kohnen and Murchey, 1995), has about 7 to 24 ppm Ni, and associated shale there has 38 to 65 ppm Ni (Karl, 1984). No analyses of local graywackes were found in published literature, but Bouse and others (1996) found 20 to 67 ppm Ni in similar Coast-Range graywacke in the Sacramento River watershed.

Published studies of the processes of release of Ni from bedrock to soil, sediment, and water within the south Bay area were not found during the present literature search, but processes of release of this element from Ni-rich serpentinite have been studied in other places. Schreier (1987) reported that high dissolved Ni content in water in a stream in Washington was associated with high concentrations of suspended serpentine fibers. Where serpentine

minerals are weathered in intensely leached soils in northern California and southern Oregon, Hotz (1964) and Foose (1992) found Ni contents in the soils up to 17,000 and 14,000 ppm, respectively. Foose (1992) showed that the Ni is closely associated with Fe oxides. Gasser and Dahlgren (1994) and Gasser and others (1995) studied natural serpentinitic soils from Tahoe National Forest, California, with about 4700 to about 8900 ppm (80 to 151 μmol/g) total Ni. Iron oxides had especially high Ni contents, and laboratory experiments with these soils suggested that about 10 percent of adsorbed Ni was present in exchangeable form (Gasser and Dahlgren, 1994). Release of Ni from the soils increased with decreasing solution pH, suggesting that short-term Ni release was dominated by desorption (Gasser and others, 1995). The majority of the Ni measured in these studies evidently is associated with fine soil particles.

Selenium

The soils analyzed by Boerngen and Shacklette (1981) were reported to contain Se in concentrations of 0.7 ppm in Gilroy, 0.4 ppm in Palo Alto, and less than 0.1 ppm in San Mateo County. These values compare with a nationwide geometric mean of 0.26 ppm Se and are within the highest, second highest, and lowest of five ranges of Se contents reported Shacklette and Boerngen (1984). Scott (1995) reported Se values up to 4 ppm in sediment Mountain View. Only 16 of 108 samples tested for Se had detectable Se (detection limits ranged from 0.2 to 4 ppm), and Scott did not calculate an average Se concentration for the samples. Kleinfelder, Inc. (1995) reported less than 1 ppm Se in most samples collected near the Guadalupe River. Only three samples had detectable Se, and the concentrations reported for those were 8, 2, and 2 ppm.

By analogy with other areas, bedrock units and soils in the south Bay area might be expected to contain high concentrations of Se. Elevated levels of Se in the San Joaquin Valley, California, have been attributed in part to bedrock sources in marine shales by Barnes (1986), or, alternatively, to bedrock concentrations that are a result of the same processes that produced the mercury mineralization at New Idria (Tidball and others, 1990). Bedrock units in the Santa Clara Valley area include both marine shales like those adjacent to the San Joaquin Valley (Wagner and others, 1990) and mercury sulfide ores like those at New Idria (Bailey and Everhart, 1964), so the occurrence of sources of Se-rich rocks surrounding the Santa Clara Valley is a possibility.

No published studies of processes controlling Se transport in the south Bay area were found in the present search. Studies in the San Joaquin Valley watershed have shown that Se is released from bedrock units by oxidation during weathering and that it accumulates in soils in water-soluble salts (Barnes, 1986; Sylvester, 1990). Barnes (1986) noted that areas in which Se has accumulated to high levels are those where the mean annual precipitation is less than 12 inches. The rainfall in the south Bay area may be high enough to prevent accumulation of Se within the soils. Where Se is mobilized, Barnes (1986) and Sylvester (1990) suggested that it is moving as dissolved or sorbed selenate.

Arsenic

Boerngen and Shacklette (1981) reported As concentrations of 8.2, 6.0, and 9.2 ppm in soils from Gilroy, Palo Alto, and San Mateo County, respectively. These three analyses are higher than the nationwide geometric mean of 5.2 ppm As and are within the second highest and the middle of five ranges of As contents reported by Shacklette and Boerngen (1984). Scott (1995) reported As values from 0.2 to 5.5 ppm in sediment from Mountain View. Of the 108 samples in Scott's study that were tested for As, 95 had detectable amounts, and she reported an arithmetic average of 2.86 ppm As for those samples. Kleinfelder, Inc. (1995) reported values from 1 to 55 ppm As in samples collected near the Guadalupe River. Most samples had less than 10 ppm, and about 10 percent had less than 1 ppm As.

Of the thirteen shale samples from within the south Bay watershed analyzed by Burnett (1965), none were reported to contain detectable As. Mason and Moore (1982) estimated that average shale contains 13 ppm As.

Welch and others (1988) found that high concentrations of As throughout the western United States are associated with four geochemical environments: 1) volcanic rocks, 2) alluvial and lacustrine deposits, especially in semiarid areas where the sediment is derived from volcanic rocks, 3) geothermal systems, and 4) uranium- and gold-mining areas. None of these geochemical environments is particularly common in the south San Francisco Bay area.

Processes of release of As from bedrock units evidently have not been studied in the south Bay region. Welch and others (1988) showed that understanding the release of As to groundwater is complicated by the variety of possible As species. Dissolution of As-bearing minerals commonly involves oxidation, but As concentrations in solution depend strongly upon the varieties of complexing and competing ions present and upon the availability of particle surfaces, especially those of Fe oxides.

STREAM AND LAKE WATERS AND SEDIMENT

Surface waters in the Santa Clara Valley have relatively low dissolved solids (Iwamura, 1995), and the water itself generally contains relatively small amounts of trace elements, but measurable concentrations have been reported in several places. Stream-bottom materials also have been analyzed in a few places. The trace-element composition of suspended sediment in local streams evidently has not been studied in detail.

Nickel

Kleinfelder, Inc. (1995) reported values from 57 to 250 ppm Ni in ten samples of stream sediment collected from the Guadalupe River in July 1994. All samples had detectable Ni, and all but one had Ni contents higher than 100 ppm.

Silvey (1971) reported that samples of stream water collected from 1960 to 1966 had dissolved Ni concentrations from 1.9 to 5.4 µg/L in Coyote Creek near Madrone and up to 3.5 µg/L in Alameda Creek near Niles. Samples of water collected from springs in Santa Clara County from 1963 to 1968 had Ni concentrations up 18 µg/L with 13 of 14 samples containing detectable Ni (Averett and others, 1971). Averett and others (1971) also reported Ni contents of stream waters from 15 sites; most samples contained detectable Ni, and four had more than 20 µg/L. Samples collected in November 1967 were the highest, with Ni concentrations reported to be 234 and 257 µg/L in Guadalupe Creek and Arroyo Calero Creek, respectively. Sylvester (1986) reported Ni concentrations in samples of stream water collected from 1979 to 1981 from eleven sites in southwestern Santa Clara County. The concentration of Ni in most water samples was reported as "0" or as "not detected." One sample had a reported dissolved Ni content less than 200 µg/L, one had 4 µg/L, and one sample each from Guadalupe River at Alamitos Recharge Facility in San Jose and Los Gatos Creek in Los Gatos had a reported value of 100 µg/L.

Averett and others (1971) reported analyses of water samples collected from 1963 through 1969 from 5 reservoirs and percolation ponds. Dissolved Ni was detected in all samples and ranged from 1.9 to 22 µg/L; the highest value was from Anderson Reservoir. Surface water in the central part of Calero Reservoir collected from 1981 to 1983 was reported by Clifton and Gloege (1987) to contain concentrations of dissolved Ni of 6, 5, less than 50, and less than 10 µg/L.

Iwatsubo and others (1988) reported that water collected in 1979 and 1980 from Los Gatos Creek above Lexington Reservoir had dissolved Ni contents of 4, 2, and less than 50 µg/L. Dissolved Ni in water samples collected in 1979 and 1980 from four sites within Lexington Reservoir was reported to be not detected or less than 50 µg/L. Taylor and others (1993) collected samples of water from Los Gatos Creek above and below Lexington Reservoir in 1985 and 1986, following a large fire and flood. They reported that dissolved Ni concentrations were "low" and not significantly higher than in samples collected before the fire.

Gunther and others (1991) compiled data from fifteen samples of storm runoff collected at three sites in their "open" land-use category in Santa Clara and Alameda counties. Twelve of the fifteen samples had detectable Ni, and Gunther and others (1991) calculated an arithmetic average Ni content of 17.67 µg/L.

No specific studies of the composition of suspended sediment in the south Bay area were found in the literature search for this report. Gunther and others (1987) reported data on Ni in the San Joaquin River for January 1984 through December 1986 and in the Sacramento River in September 1986. The estimated average concentrations of dissolved and total Ni were 1.7 to 2.3 µg/L and 12 µg/L, respectively, in the San Joaquin River and 0.670 µg/L and 2.033 µg/L, respectively, in the Sacramento River. The San Francisco Estuary Regional Monitoring Program for Trace Substances (1994) reported dissolved and near-total Ni concentrations for 1993 samples of 0.89 to 1.26 µg/kg and 2.62 to 5.64 µg/kg, respectively, in the San Joaquin River and 0.40 to 0.71 µg/kg and 1.37 to 3.71 µg/kg, respectively, in the Sacramento River. These data indicate that most of the Ni is on and in particles.

Selenium

Sylvester (1986) reported total Se concentrations of "0" in 40 samples of stream-bottom material collected from 1979 to 1981 from eleven sites in southwestern Santa Clara County. Kleinfelder, Inc. (1995) reported less than 1 ppm Se in all ten samples of stream sediment collected from the Guadalupe River in July 1994.

Iwatsubo and others (1988) did not detect Se in water collected in 1979 and 1980 from Los Gatos Creek above Lexington Reservoir and from three sites within Lexington Reservoir; the reported values for dissolved Se are all "0," less than 1, or less than 10 µg/L. Taylor and others (1993) collected samples of water from Los Gatos Creek above and below Lexington Reservoir in 1985 and 1986, following a large fire and flood, and reported that dissolved Se concentrations were "low" and not significantly higher than in samples collected before the fire.

In the San Joaquin River, the estimated average concentrations of dissolved and total Se were reported to be 0.777 and 0.6 to 1.1 µg/L, respectively (Gunther and others, 1987). The San Francisco Estuary Regional Monitoring Program for Trace Substances (1994) reported dissolved and total Se concentrations for 1993 samples of 0.31 to 0.77 µg/kg and 0.24 to 0.74 µg/kg, respectively, in the San Joaquin River and 0.11 to 0.27 µg/kg and 0.12 to 0.34 µg/kg, respectively, in the Sacramento River. Most of the Se there is carried in solution as selenate (Cutter, 1989).

Arsenic

Sylvester (1986) measured As concentrations in both stream water and stream-bottom materials collected from 1979 to 1981 from eleven sites in southwestern Santa Clara County. Reported As content of the water samples ranged from "0" to 4 µg/L, and the As content of the stream-bottom materials ranged from 3 to 16 ppm. Some spatial variability is evident in the data; the reported values of As in stream-bottom materials was 4 to 10 ppm in Los Gatos Creek, 3 to 14 ppm in Coyote Creek, and 6 to 16 ppm in Guadalupe Creek and the Guadalupe River.

Kleinfelder, Inc. (1995) reported values from 4 to 8 ppm As in ten samples of stream sediment collected from the Guadalupe River in July 1994. All samples had detectable As.

Durum and others (1971) collected water samples from four Bay-area reservoirs in 1970. They reported dissolved As concentrations below their limit of detection of 10 µg/L for all of those samples. Surface water in the central part of Calero Reservoir collected from 1981 to 1983 was reported by Clifton and Gloege (1987) to contain concentrations of dissolved As of 1, less than 1, and less than 10 µg/L.

Iwatsubo and others (1988) reported that water collected in 1979 and 1980 from Los Gatos Creek above Lexington Reservoir had dissolved As contents of 4, 1, and less than 10 µg/L. Most water samples collected in 1979 and 1980 from three sites within Lexington Reservoir had As contents less than 10 µg/L. One sample collected in 1979 near the center of the reservoir had 3 µg/L dissolved As. Taylor and others (1993) collected samples of water

from Los Gatos Creek above and below Lexington Reservoir in 1985 and 1986, following a large fire and flood. They reported that dissolved As concentrations were "low" and not significantly higher than in samples collected before the fire.

Gunther and others (1987) reported estimated average concentrations of dissolved and total As in the San Joaquin River of 1.5 to 1.6 µg/L and 2.4 µg/L, respectively. The San Francisco Estuary Regional Monitoring Program for Trace Substances (1994) reported dissolved and total As concentrations for 1993 samples of 1.43 to 1.98 µg/kg and 1.83 to 2.32 µg/kg, respectively, in the San Joaquin River and 1.05 to 1.44 µg/kg and 1.31 to 1.60 µg/kg, respectively, in the Sacramento River. Significant proportions of the As evidently are carried both in solution and associated with particles.

GROUND WATER

A few published reports are available on trace elements in uncontaminated groundwater in the south Bay area. In addition, water quality data were searched for all public drinking water sources in Santa Clara County for the years 1990 through 1997. Although these data are from sites assumed to be uncontaminated, they are relatively recent samples with no guarantee that trace elements are present at natural levels. Also, some of the Ni could be from metals in pipes or pump parts.

Nickel

Averett and others (1971) summarized data for Santa Clara Valley well samples taken from 1967 through 1969. Of 81 samples taken from the Coyote Valley basin north, 35 had detectable amounts (greater than 0.3 µg/L) of dissolved Ni. Samples from the northern part of the county all had less than 3 µg/L Ni; some wells to the south, near serpentinite outcrops, had higher Ni contents, with one well from the Santa Teresa area having a reported Ni concentration of 13 µg/L in 1968.

Water quality data from drinking water sources in Santa Clara County north of the Llagas basin from 1990 through 1997 include 29 reports of detectable Ni. Detection limits ranged from 1 to 50 µg/L, and reported values ranged from 2.4 to 26 µg/L Ni. Five samples were reported to contain more than 10 µg/L Ni: three samples from wells in Los Gatos, one sample from a well in San Jose, and one sample, with the highest reported concentration, from a well in an area of siltstone and shale bedrock in the Santa Cruz Mountains.

Selenium

Moll and others (1980) summarized historical ground water quality data for 96 wells throughout the major valley areas of Santa Clara County. Wells sampled from 1971 to 1977 were tested for Se, and the results for all of the tests included in this summary were reported as "0.00." Alvarez and others (1988) summarized the results of testing of 955 private wells in Santa Clara County for inorganic chemicals and reported that two wells in San Jose were found to have total (unfiltered) selenium contents higher than 10 µg/L. One well had 11 and 14 µg/L Se on two dates, and another well had 19 µg/L Se on one date; each well was reported to have less than 10 µg/L Se at other times.

Water quality data from drinking water sources in Santa Clara County north of the Llagas basin from 1990 through 1997 include 80 reports of detectable Se. Detection limits ranged from 0.005 to 50 µg/L, and reported values ranged from 0.75 to 12 µg/L Se. Nearly all samples had less than 10 µg/L Se, and most containing detected Se are from the central part of the valley (San Jose Water Company wells). The single sample with more than 10 µg/L Se is from a well in the Evergreen/Edenvale area.

Arsenic

Moll and others (1980) reported results of analyses for As in waters from 5 wells sampled in 1971; all five results were reported as "0.00." Alvarez and others (1988) summarized the results of testing of 955 private wells in Santa Clara County for inorganic chemicals and reported that the only two wells with As concentrations above 50 µg/L were in Morgan Hill and Gilroy, in the southern part of the county.

Welch and others (1988) compiled the results of more than 7000 As analyses of ground waters from the western United States. All of the samples they included from Santa Clara and Alameda counties had As concentrations less than 10 µg/L.

Water quality data from drinking water sources in Santa Clara County north of the Llagas basin from 1990 through 1997 include 68 reports of detectable As. Detection limits ranged from 0.002 to 100 µg/L, and reported values ranged from 0.38 to 200 µg/L As. Most samples containing detected As are from the central and southern parts of the valley. Three samples were reported to contain more than 10 µg/L As: one sample from an inactive well in Milpitas had 13 µg/L in 1991, and two wells in Santa Clara were reported to contain 110 and 200 µg/L As in 1993.

Welch and others (1988) suggested that elevated As concentrations in ground water could result from reactions between iron oxides with adsorbed As and water that is chemically reduced because of abundant interbedded sedimentary organic matter. These conditions are not common in near-surface or subsurface sediment within the Santa Clara Valley (Iwamura, 1995), but they may be more widespread within late Cenozoic estuarine sediment beneath the San Francisco Bay (Atwater and others, 1977).

SAN FRANCISCO BAY

A large amount of information is available on present levels of trace elements within the San Francisco Bay, including analyses of bay water, sediment, and biota. The Bay is a very complex system, with important variations in both space and time (e.g., Cloern and Nichols, 1985; Walters and others, 1985). It also has been extensively modified by human activities, so it is difficult to assess the amounts of trace elements that represent natural background levels.

Nickel

Recent samples of San Francisco Bay water contain up to 8 µg/L Ni in the southern part of the south Bay (Phillips, 1987). The amount of Ni generally decreases northward to about 1 µg/L near the Golden Gate, with lower values in offshore waters. Flegal and others (1991) reported similar patterns and argued that the high Ni content of water in the south Bay is largely anthropogenic.

The San Francisco Estuary Regional Monitoring Program for Trace Substances (1994) reported dissolved and near-total Ni concentrations in 1993 samples of south Bay water ranging from 1.75 to 3.56 µg/kg and from 2.40 to 10.37 µg/kg, respectively, at four sites on three sampling dates. Near-total Ni generally was lower in the south Bay than in the northern estuary, but the average dissolved Ni was higher in the south Bay than in other parts of the estuary. Within the south Bay, Ni concentrations generally decreased from south to north. Dissolved Ni was higher in the south Bay in March than in May or September, suggesting that local runoff may be a source of Ni.

Sediment samples collected at four sites in the south Bay (as defined in this report) on two dates in 1993 contained 51.45 to 95.80 ppm near-total Ni (San Francisco Estuary Regional Monitoring Program for Trace Substances, 1994). The concentration of Ni was highest in fine-grained sediment throughout the Bay, and it was higher in the south Bay and the northern estuary than in the central Bay. Within the south Bay, the concentration was higher or slightly higher in March than in September.

Sediment throughout the San Francisco Bay generally contains nearly 100 ppm Ni (Phillips, 1987), and much of this is believed to be from natural geological sources (San Francisco Estuary Regional Monitoring Program for Trace

Substances, 1994). This view is supported by several studies. In a test of methodology for evaluating sites that are contaminated, Chapman and others (1986) used the average composition of sediment samples from a site in San Pablo Bay with 81 ppm Ni as their reference station to represent nearly natural local sediment. Hornberger and others (in press) analyzed cores from the north Bay and reported Ni concentrations of about 80 ppm in the sediment deposited before the influence of human activities. They noted that this concentration is higher than that in most U.S. coastal sediment and attributed the natural Ni levels here to the presence of ultramafic rocks and graywacke in the watershed. Bouse and others (1996) found similar high concentrations (92 ppm Ni; Robin Bouse, 1998, oral communication) in the deepest part of an undated core collected in the south Bay, near the San Mateo Bridge, and interpreted that to represent the natural background composition at that site.

Most of the natural input of Ni to the Bay is particulate; natural sources of dissolved Ni include direct input from rivers and exchange from particles (Eaton, 1979b). Other sources, which evidently are less than river inputs, include surface runoff (Gunther and others, 1991) and atmospheric deposition (Papp, 1998). Flux from previously deposited Ni-rich sediment also is a potentially large source of Ni. Once dissolved, Ni^{2+} probably is the dominant inorganic species of Ni in south Bay waters; some Ni in modern samples also is complexed by strong organic ligands (Donat and others, 1994). Ni can be precipitated mainly with Fe oxides and organic compounds (Eaton, 1979a).

Post-depositional changes in Ni-bearing sediment, including degradation of organic matter, reduction of Mn, and formation of soluble sulfide complexes, evidently release Ni to pore fluids (Rivera-Duarte and Flegal, 1994, 1995; Flegal and others, 1996). These fluids could reenter Bay waters due to diffusion and irrigation involving animal burrows (Hammond and others, 1985) or by compaction or resuspension of the sediment. Kuwabara and others (1996) showed that the flux of Cd and Cu between sediment and the water column in the Bay changed directions seasonally, and more work will be needed to understand and quantify any flux of Ni from the sediment to the Bay.

Selenium

Water samples from the south Bay contained 257 to 323 ng/L (3.26 to 4.09 nmol/L) dissolved Se in April 1986 and 137 to 358 ng/L (1.74 to 4.54 nmol/L) dissolved Se in September 1986 (Cutter, 1989). Concentrations were highest in the southern part of the Bay and decreased northward, and Cutter (1989) argued that these high Se concentrations were largely anthropogenic. Most of the dissolved Se was present as "organic selenides" (Se II+0) in the April survey and as selenate in September. Cutter (1989) also reported Se concentrations in suspended particles of 2 to 24 ng/L (0.03 to 0.31 nmol/L) in April and 7.9 to 26 ng/L (0.10 to 0.33 nmol/L) in September.

The San Francisco Estuary Regional Monitoring Program for Trace Substances (1994) reported that samples of south Bay water collected at four sites on three dates in 1993 had concentrations of 0.15 to 0.51 µg/kg dissolved Se and 0.131 to 0.406 µg/L total Se. The authors noted that the data for samples collected in March, 1993, which include the highest and lowest values of dissolved Se listed above, exceeded quality assurance limits and should be used with caution. The ratio of dissolved to total Se was higher and less variable than that for other trace elements throughout the San Francisco Bay. The concentrations of Se were higher in the south Bay than in the rest of the estuary in March, but Se was higher in the northern estuary by September. In the south Bay, dissolved Se decreased with increasing salinity, especially in March, suggesting that local runoff was a more important source of dissolved Se than year-round sources.

Chapman and others (1986) reported Se contents less than 3 ppm in sediment from all three of their sites, including the site in San Pablo Bay that they interpreted as having the most nearly natural composition and both of their contaminated sites in the south Bay. Johns and others (1988) measured Se in fine-grained south Bay sediment as 0.15 ppm at one site and ranging from 0.2 to 0.55 ppm in five samples collected from another site. The site with the high values of Se in sediment also had high Se in molluscs, which Johns and others (1988) suggested might represent regional enrichment or patchiness of bioavailable Se in the south Bay. The concentrations of Se in sediment samples from the north Bay generally were comparable to those from the south Bay.

Sediment samples collected at four sites in the south Bay (as defined in this report) on two dates in 1993 contained 0.23 to 1.27 ppm total Se (San Francisco Estuary Regional Monitoring Program for Trace Substances, 1994). The concentration of Se was higher in in the northern estuary than in the south Bay and it was higher in September than in March. The concentration also was highest in fine-grained sediment in September, but not in March.

The biogeochemistry of Se is complex, partly because it occurs in several different oxidation states and because it is an essential trace element in plants and animals (Phillips, 1987). Cutter (1989) showed that an important source of Se in the north Bay is from the San Joaquin River drainage and that the relationship of different Se species to nutrients and salinity is too complex to be explained by simple dilution with sea water. Much of the Se that enters the Bay from rivers is dissolved as selenate. Important natural processes affecting Se species probably include dissolution of particulate Se and oxidation of selenite to selenate (Cutter, 1989).

Arsenic

The San Francisco Estuary Regional Monitoring Program for Trace Substances (1994) reported that 1993 samples of south Bay water collected at four sites on three dates had concentrations of 1.75 to 3.80 µg/kg dissolved As and 1.49 to 4.37 µg/L total As. The range of As concentrations throughout the Bay was less than that for most trace elements, and the ratio of dissolved to total As was fairly high. The south Bay had higher concentrations than the rest of the estuary, and this difference increased from March to September, suggesting a year-round, local source of As in the south Bay.

Fine-grained sediment sampled at two localities in the south Bay contained mean total As in concentrations of 6.0 and 8.5 ppm and acid-extractable As of 1.8 and 2.5 ppm (Johns and Luoma, 1990). The total As concentrations were lower than those in similar samples from the north Bay and comparable to total As contents of sediment in uncontaminated estuaries in the United Kingdom.

Sediment samples collected at four sites in the south Bay (as defined in this report) on two dates in 1993 contained 7.93 to 14.15 ppm total As (San Francisco Estuary Regional Monitoring Program for Trace Substances, 1994). The concentration of As was higher in parts of the central Bay than in the south Bay, and it was higher in most places in March than in September. The concentrations also were highest in the finest sediment, but As content was significantly correlated with grain size only in the September samples.

Arsenic enters the Bay from river sources in both dissolved and particulate forms (Gunther and others, 1987). Dissolved As occurs in the Bay in several different inorganic and organic species (Phillips, 1987), and marked seasonal variation in the abundances of these species has been shown in other areas (Riedel, 1993). Dissolved As can be readily adsorbed by Fe oxides, or those oxides can release sorbed As, especially in reducing conditions, either before or after deposition in bottom sediment (Welch and others, 1988). The factors controlling dispersal and fixation of As in the San Francisco Bay are likely to be complex and presently are not well described in published literature.

CONCLUSIONS

The bedrock geology of the south Bay includes some rock units that are known to contain relatively high concentrations of Ni and other rock types that contain relatively high concentrations of Se in other areas; a major source of As evidently has not been identified. The published analyses found in this literature search do not provide enough information to estimate average trace-element contents of south Bay soils for the purpose of predicting natural loadings from runoff to the Bay; more analyses are needed of local soils developed on a variety of bedrock types and of sediment in local streams. Future analyses of samples from well dated, deep cores of Bay sediment deposited before the influence of human activities would hold great promise for determining the natural background concentrations of trace elements within the Bay itself.

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